SPENT AUTOMOTIVE CATALYTIC CONVERTERS FROM END-OF-LIFE VEHICLES AS A VALUABLE SOURCE OF PLATINUM-GROUP METALS

Ana Radojević, Jelena Jordanović, Tanja Kalinović, Jelena Kalinović, Snežana Šerbula

University of Belgrade, Technical Faculty in Bor, Bor, Serbia

(REVIEW PAPER)
UDC: 546.91:[628.4.037:54-44
DOI: 10.5937/savteh2502005R

Every year, more than 5 million end-of-life vehicles (ELVs) in Europe must be properly managed, otherwise, inadequate handling will result in environmental pollution. From an economic perspective, approximately 6 million tonnes of valuable materials are lost annually through ELVs. Platinum (Pt), palladium (Pd), and rhodium (Rh) belong to the platinum-group metals (PGMs) and represent an active component of automotive catalytic converters, which are used for the efficient catalytic conversion of exhaust gases into less harmful compounds. The automotive industry is one of the most resource-intensive sectors. As the number of motor vehicles increases, the global demand for the mentioned precious metals is constant, as they are also listed among the critical ones. Moreover, the PGMs are also required in green technologies related to vehicle electrification, green energy, hydrogen production, etc. Due to their high PGM loadings, spent automotive converters are valuable secondary materials that could be exploited at lower prices and with less ecological impact on the environment compared to the extraction of PGMs from ores. Numerous agents are proposed in the literature for the leaching of PGMs, among which cost-effective, environmentally friendly, and sustainable leaching solutions are preferable. The article aims to emphasise the importance of recycling PGMs from secondary raw materials, primarily spent automotive catalytic converters (ACCs), and to provide an overview of the key aspects of the current supply and demand challenges related to PGMs.

Keywords: platinum-group metals, end-of-life vehicles, automotive catalytic converters, recycling

Introduction

The development of automotive catalytic converters (ACCs), also known as three-way catalysts (TWCs), with the aim of reducing exhaust emissions, was considered one of the most significant environmental achievements of the 20th century [1]. Therefore, since 1993, all motor vehicles have been supplied with catalytic converters to reduce the emission of incomplete fuel combustion products, carbon monoxide (CO), hydrocarbons (C_nH_m), methane (CH_4), and nitrogen oxides (NO_x), according to the proposed levels by converting them into less harmful compounds. The precious metals, such as platinum (Pt), palladium (Pd), and rhodium (Rh), represent active components of ACCs in the process of the triple conversion: oxidation of CO and C_nH_m to CO_2 and H_2O and reduction of NO_x to N_2 [1,2]. These metals are referred to as platinum-group metals (PGMs), together with iridium (Ir), ruthenium (Ru), and osmium (Os), with Pt being the most important metal in the group. Today, the great importance of PGMs in modern technologies, electronics, advanced chemistry, medicine, agriculture, explosives manufacturing, aerospace, decarbonisation, energy storage, and everyday use (e.g., jewellery) is recognised due to their excellent electrical and chemical properties, resistance, and stability at high temperatures. In recent years the production of green hydrogen has become crucial for net-zero emissions as global interest focuses on clean energy technologies. PGMs improve the performance of hydrogen fuel cells, allowing them to operate at higher efficiencies and reliability, making hydrogen technology more viable for widespread use [3-8].

One of the most important events that reshaped the global trade market occurred in 2010 when China reduced its production of rare earth elements (REEs) by 25% and cut export quotas for REE products by 37%. As China was the world's leading producer of rare earth minerals, these measures led to a sharp increase in prices. For instance, the export price for neodymium oxide surged from $25 per kilogram in early 2010 to a peak of $340 per kilogram in July 2011. This significant price increase drew global attention and raised concerns about the security of critical materials supply [9]. Europe responded more promptly than other regions to the economic importance and supply risk of PGMs and included them in Critical Raw Materials (CRMs). The list of CRMs, drawn up in 2008 as a priority measure of the EU Raw Materials Initiative, is updated at least every three

*Author address: Ana A. Radojević, University of Belgrade, Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, Serbia
E-mail address: aradojevic@tfbor.bg.ac.rs
The manuscript received: March 26, 2025
Paper accepted: July 7, 2025

years, considering the current production, demand, and technological trends [10]. CRM are materials that have a high economic importance and supply risk, whereby their reliable and unrestricted access is important for the European industry. In 2011, the first list consisted of 14 CRMs [11], while the fifth list was expanded to 34 CRMs in 2023 [12], with PGMs being considered as critical raw materials from the outset [10]. In the most recently published list, PGMs were also categorised as "strategic raw materials" (SRMs), indicating materials that are important for technologies that support the green and digital transitions [12]. Pt, Pd, and Ir are on the "long list of metals within reach", representing metals in key applications for the energy transition in the EU [13]. The challenges related to the availability of raw materials are also important for the United States (U.S.), especially for the transition to a more sustainable energy supply. The U.S. Department of Energy has also identified several critical technologies related to energy challenges, such as energy storage, hydrogen and fuel cells, wind, solar, geothermal and bioenergy, electric vehicles, and materials essential to the green transition, such as rare earths and PGMs [14]. Due to the current trend towards the electrification of vehicles, the automotive sector in Europe is expected to become the largest consumer of CRMs soon [15].

The end-of-life vehicles Directive 2000/53/EC [16] sets measures aimed primarily at preventing the generation of waste from vehicles. It also aims to promote the reuse, recycling, and other recovery methods for end-of-life vehicles (ELVs) and their components. The overall objective is to minimise the amount of disposed waste while improving the environmental performance of all economic actors involved in the life cycle of a vehicle, in particular those directly involved in the handling of ELVs, which is also in accordance with the general objective of the circular economy. The transition from the traditional linear economy to the circular economy is a systematic and serious change that will affect many aspects of the economy and modern society. In the new Circular Economy Action Plan, the European Commission (EC) proposes measures to improve the circular economy in the automotive sector. These measures relate to the development, production, and disposal of vehicles, improving access to resources, and contributing to the EU's environmental and climate goals. The proposed measures are expected to generate a net gain of €1.8 billion by 2035, create new jobs, and generate profits in the recycling and waste management sector. In addition, the export of less roadworthy vehicles from the EU will be prevented, which will reduce air pollution and associated health risks in countries that import old and used vehicles [15,17]. The new perspectives of the zero-waste initiative will ensure a good quality of life in many aspects. At the same time, vehicle production will be guided by increasing energy efficiency with lower emissions [18].

The recycling of PGMs also contributes to the achievement of the United Nations Sustainable Development Goals (SDGs) by improving environmental quality and overall well-being. In particular, it supports SDG 3 ("Ensure healthy lives and promote well-being for all at all ages"), SDG 9 ("Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation"), and SDG 11 ("Make cities and human settlements inclusive, safe, resilient, and sustainable") [19].

The EU's industry and economy are resource-reliant on imports from the international markets for many important raw materials, including PGMs, while the supply of many CRMs is highly concentrated. For example, China provides 100% of the EU's supply of heavy REEs, South Africa provides 71% of Pt and an even higher share of Ir (93%), Rh (81%), and Ru (94%). While the EU has domestic production of certain CRMs, the risk of supply chain disruptions due to global geopolitical events poses a significant threat to the already vulnerable EU market. Investing in the recycling industry of ACCs would help ensure a secure and independent supply of CRMs within the EU, reducing reliance on imports of critical materials such as PGMs and maintaining the EU's industrial competitiveness. Additionally, the supply risks are intensified by the lower recycling rates, which currently stand at around 50–60% globally [20,21]. In 2024, the global primary and secondary supply of Pt amounted to 220.6 tonnes, which was lower than the total demand of 244.8 tonnes, primarily demanded by the automotive industry and jewellery production. A similar supply-demand gap was observed for Pd (required for the automotive industry and electronics production), with a deficit of 15.6 tonnes and 1.2 tonnes for Rh (automotive and chemical industry). Supply constraints were also globally evident for Ru (chemical industry and electronics production), and Ir (for electrochemical applications) [22]. Although the PGM loadings in ACCs are low, mostly in the range of 3.2–9.4 g for an average passenger car weighing 1,000–1,800 kg, it takes up to six months and 10–40 tonnes of primary ores to produce about 31 kg of Pt [23].

This paper aims to highlight the importance of spent automotive catalytic converters from end-of-life vehicles as valuable secondary materials for the recovery of PGMs, with special emphasis on hydrometallurgy (i.e. leaching), since PGM-containing ores are non-renewable metal sources and the global primary production of PGMs is limited and cannot meet the total demand in various applications.

Demand for PGMs in Green and Other Technologies

Regarding the global demand for Pt in 2023, the automotive industry was in first place (104 tonnes), followed by the jewellery industry (42.3 tonnes), the glass industry (24.1 tonnes), and the chemical industry (20.1 tonnes). The application in pollution control, dentistry, and biomedical technologies required around 17 tonnes of Pt, followed by demand from the electrical and electronics industry (6.1 tonnes) and the oil industry (5.4 tonnes). In the period since 2021, the global demand for Pt has

increased, especially in the automotive sector. The automotive industry accounts for by far the largest demand for Pd, with 272 tonnes of 322.6 tonnes of the total global demand for Pd in 2023, followed by the chemical industry (16.9 tonnes) and the production of electrical and electronic equipment (15.9 tonnes). In 2023, the total demand for Rh amounted to 34.7 tonnes, with the automotive industry being the sector that used the largest amount of Rh (30.8 tonnes). The total primary supply of Rh in 2023 was 28.7 tonnes, slightly lower than the total global demand of 31.3 tonnes, mostly demanded in the chemical industry (13.3 tonnes) and in the production of electrical and electronic equipment (9.6 tonnes). The total primary supply of Ir corresponded to the total demand (7 tonnes), which was mainly required by the electrochemical industry (3.2 tonnes) [8].

In the course of 2023, the total demand for Pt in Europe amounted to almost 50 tonnes [8], the largest share of which was required in the automotive industry (around 60%) (Figure 1). Due to the new emissions legislation in Europe (the Euro 6e standard will be replaced by the Euro 7 standard for all new light vehicles, regardless of fuel type or powertrain, in July 2025), as well as in China and India, the global Pt demand is expected to increase by 11% [24]. In the case of Pd, the total demand in Europe was more than 70 tonnes [8], with about 90% being required for the automotive industry (Figure 2) during 2023.

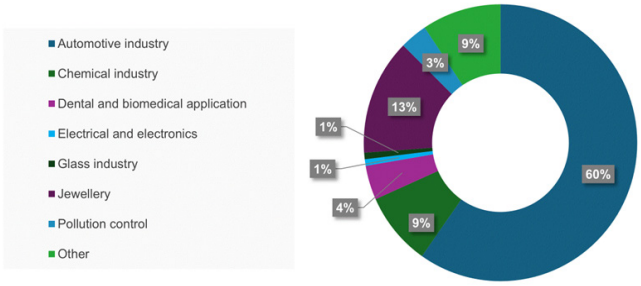


Figure 1. Total demand (%) for Pt in different sectors in Europe during 2023 [8]

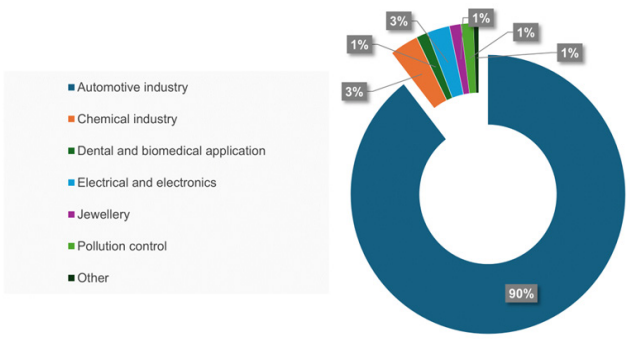


Figure 2. Total demand (%) for Pd in different sectors in Europe during 2023 [8]

In addition to the production of catalysts for the automotive industry, PGMs are used in a variety of environmentally friendly industrial applications, e.g. in the production of glass fibres, which are important for the production of renewable energy; copper foils for lithium-ion batteries and fuel cells, to reduce global CO_2 emissions; biofuels and synthetic fuels that could replace fuels of fossil origin, etc. [8,13]. In terms of the demand for PGMs in environmentally friendly applications, the highest demand is for glass fibre production, where Pt-Rh alloys are used in the equipment for the extrusion of molten glass into fine filaments. Very large quantities of glass fibres are also required in the renewable energy sector for the manufacture of blades for wind turbines and as a substitute for aluminium in frames for photovoltaic systems. It is estimated that up to 10,000 tonnes of glass fibres are required for 1 GW of wind power capacity, while more than 3,500 tonnes are needed for photovoltaic frames to generate the same amount of energy [8]. Pt is the key metal for electrolysers used in hydrogen production with an optimisation potential of 80–90% compared to current quantities. Pt and Ir are among the metals in the group of medium pull whose transition-specific demand by 2050 will be in the range of 40–100% of their 2020 demand, while Ir is expected to have over 50% of its demand in clean energy technologies by 2030 [13].

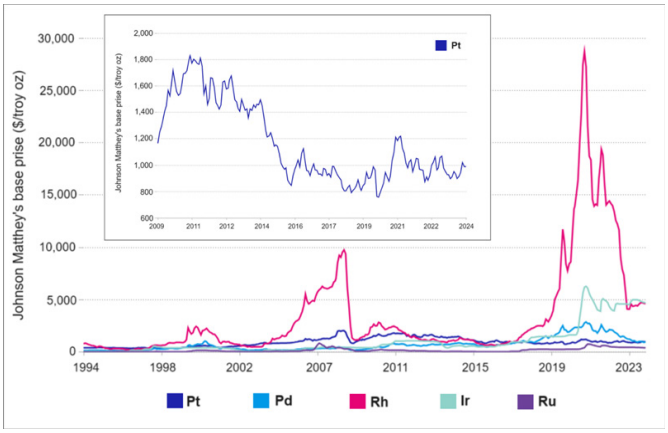


Figure 3. Variations of the base price of PGMs ($/troy oz) in the period 1994–2024 and the base price of Pt ($/troy oz) in the period 2009–2024 (note: 1 troy oz = 31.1035 g) [25]

The consumption of Pd and Ru used in electronic components was particularly high in the period 2020–2021, which was driven by the increased demand for the production of computers, hard drives, mobile phones, and other devices, due to the global move towards home-based work and activities in major economies during COVID-19 lockdowns. Although the demand for electrical devices has steadily declined over the past two decades due to the miniaturisation of electronic components, the total consumption of PGMs in electronics was the highest in 2021 (almost 40 tonnes), followed by a decline of a quarter between 2021 and 2023 (just over 28 tonnes) [8]. According to Johnson Matthey's base price [25], the prices for all PGMs, especially for Rh, increased after a relatively stable period around 2020 (Fig-

ure 3). Using an empirical approach, Gleich *et al.* [26] concluded that the driving factor of the nominal Pt price is secondary production, while Fernandez [7] found that the real price of PGMs was strongly positively correlated with the global annual production and consumption in the U.S. over the period 1930–2014.

Sources of Platinum-group Metals

Primary Sources of PGMs

The average concentrations of PGMs in the lithosphere are very low, mostly in the range of 0.001–0.005 g t^{-1} for Pt, 0.015 g t^{-1} for Pd, 0.0001 g t^{-1} for Rh and Ru, 0.005 g t^{-1} for Os, and 0.001 g t^{-1} for Ir [27]. In ores, PGMs are usually found as accompanying metals of oxide and sulphide nickel ores, sulphide copper and oxide chromium ores, and accompanying metals of other precious metals, such as gold. The primary ores contain PGMs from 1 to 2 g t^{-1}, up to 10 g t^{-1}, compared to copper-nickel ores, in which PGMs are present in the much lower range of 0.1–1 g t^{-1} [28-30].

Today, the largest deposits of PGM-bearing minerals are located in South Africa (Bushveld Igneous Complex), Russia (Norilsk and Pechenga), Canada (Sudbury Complex), the U.S. (Stillwater), and Zimbabwe (Great Dyke) [4,6,8,30,31]. Around 92% of the Pt and 80% of the global Rh production comes from the mines located in South Africa. Russia and South Africa are the dominant producers of Pd with a share of 40% and 37%, respectively, while Canada, the U.S., and Zimbabwe have minor contributions to the world production of PGMs. Since the 1900s, the maximum global production of PGMs (particularly of Pt, Pd, and Rh) was reached during the course of 2005, exceeding 500 tonnes [6]. According to the system dynamics model for PGMs, which takes into account the supply, market price, depletion, and ore grade, recycling, and stocks in use, Sverdrup and Ragnarsdottir [6] have suggested that the peak of PGM production from mines will likely happen between 2035 and 2050, while the peak in supply to society will occur years after that. However, it is estimated that the new significant reserves of PGMs will not be discovered soon [32], and new mines will be opened in the already active ore bodies [33].

Depending on the occurrence in the ores, the corresponding PGM grade in industrial practice may be reported as „3E" grade (Pt+Pd+Au), „4E" grade (Pt+Pd+Rh+Au), or even „6E" grade (Pt+Pd+Rh+Ru/Os+Ir+Au), with Os being reported extremely rarely [29,34]. The average grade of the estimated reserves is given in Table 1.

Table 1. The average grade of estimated reserves of platinum-group metals in the world [34]

Country	Canada	Russia	South Africa	U.S.	Zimbabwe
Grade (g t^{-1})	2.29 3E[a]	4.47 3E[a]	3.21 4E[b]	12.43 2E[c]	3.23 4E[b]

[a] 3E grade – The sum of Pt, Pd, and Au; [b] 4E grade – The sum of Pt, Pd, Rh, and Au; [c] 2E grade – The sum of Pt and Pd.

According to Mudd [29], the supply of PGMs and the classification of economic mineral resources in the coming decades will depend more on the social, environmental, political, and economic factors rather than on the geological nature or depletion of resources. Since there is no primary production of PGMs in Europe, the most important global supplier for the European market is South Africa, with 94% of Pt, Rh, Ir, and Ru, while 40% of the total share of Pd comes from Russia [12]. Although PGMs can often substitute each other in many industrial applications, the scarce supply remains, as it only shifts the problem from one metal to another, considering that the production of PGMs from mines is in the same order of magnitude [35].

The extraction of PGMs from ores, especially low-grade ores, undoubtedly has an adverse effect on the environment, with the main ecological problems being related to the generation of large quantities of solid waste from excavation, the high consumption of water and energy, the emission of harmful gaseous pollutants during smelting (e.g. sulphur dioxide), etc. [3]. The increase in PGMs content during mineral processing is achieved by flotation [28,29]. PGMs are obtained from the high-grade concentrates with an average content of 200 g t^{-1} by the conventional "matte-smelting-refining" technique [31,36]. Despite the similar grade of PGM ores to gold-bearing ores, the unit environmental cost of processing PGM ores is generally slightly higher in regard to energy consumption, moderately higher regarding greenhouse gas emissions, and slightly lower concerning water consumption, compared to gold production [37]. The growing interest in reclaiming tailings to achieve profitability is also considered, as the primary production of PGMs generates large amounts of flotation waste annually. However, flotation tailings represent a complex polymetallic matrix with a low-grade value of precious metals [34].

During the course of 2023, the total primary supply of Pt was over 180 tonnes, with more than 124 tonnes mined in South Africa and 24.3 tonnes in Russia. Zimbabwe accounted for 16 tonnes and North America for 9 tonnes of primary Pt. The data for Pd is similar to Pt in 2023 in terms of shares; 84 tonnes and nearly 73 tonnes out of 203.6 tonnes of total primary Pd supply originated from Russia and South Africa, respectively, followed by North America (26.8 tonnes) and Zimbabwe (13.3 tonnes). For Rh, mines in South Africa accounted for 17.4 tonnes out of 21.8 tonnes of the total primary supply, while only 2.2 tonnes of Rh were mined in Russia during 2023. During the same year, the total primary supplies of Ru and Ir amounted to 28.7 tonnes and 7 tonnes, respectively [8]. However, in recent years, geopolitical developments have impacted this supply chain, and European countries should take several steps to

reduce their reliance on Russian PGMs by diversifying supply sources to South Africa, Zimbabwe, and Canada, investing in alternative strategies and PGM recycling, exploring local reserves, etc.

Secondary Sources of PGMs

Since the primary production of PGMs causes vast environmental problems, it is reasonable that the recycling of converters from ELVs in order to restore Pt, Pd, and/or Rh has gained significant attention in recent years. Recovering PGMs from secondary sources such as spent converters has numerous advantages besides reducing the need for virgin PGMs: a simplified process, smaller-scale plants, lower investment and costs, a shorter production cycle, etc. [30]. The benefits of the circular economy are also expected in the context of designing and manufacturing new vehicles that can be easily dismantled and repaired during and after use [15]. Between 2019 and 2023, a significant decline in the recovered amount of Pt, Pd, and Rh from the secondary sources has been observed, showing similar changes in the global recycling rates and secondary supply of PGMs (Table 2). The amount of recycled Pt decreased by nearly 38% in the 5-year period, with the most pronounced drop observed in the jewellery sector, from 20.6 to 7.1 tonnes. For Pd, the secondary supply declined by almost 18% from 2019 to 2023. The automotive sector accounted for over 80% of secondary Pd, but its amounts decreased, contrary to the jewellery and electronics sectors, which have been stable. The secondary supply of Rh has been completely reliant on the automotive sector; however, amounts declined by almost 20% in the 5-year period. The data could reflect the decline in spent catalytic converters containing PGMs by reducing the share of vehicles intended for recycling. Along with the global transition to electric and hybrid vehicles, this trend is likely to lead to a further reduction in the recycling base for PGMs in the automotive sector, which will impact the long-term secondary supply of these metals in the market. However, outside China, the automotive scrap industry has remained at a very low level [22].

Table 2. Global secondary supply for Pt, Pd, and Rh (tonnes) in the period 2019–2023 by the main sectors [8]

Sector/Total amounts	2019	2020	2021	2022	2023
			Pt		
Automotive	43.2	36.0	38.4	37.5	32.2
EE	1.3	1.1	1.4	1.2	1.1
Jewellery	20.6	15.7	11.4	8.5	7.1
Total Pt	*65.1*	*52.8*	*51.2*	*47.2*	*40.4*
			Pd		
Automotive	90.7	83.7	89.7	84.9	72.6
EE	14.9	13.3	13.8	14.1	14.4
Jewellery	0.3	0.2	0.3	0.3	0.3
Total Pd	*105.9*	*97.2*	*103.8*	*99.3*	*87.3*
			Rh		
Automotive	11.1	10.5	11.2	10.4	8.9
Total Rh	*11.1*	*10.5*	*11.2*	*10.4*	*8.9*

EE – electrical and electronic devices.

Table 3. The total number of end-of-life vehicles and total weight (tonnes) in the European Union in the period 2008–2021 [39]

Parameter	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
Number of ELVs*	5,079	7,700	6,213	5,555	5,123	5,085	5,043	4,968	4,823	5,300	6,105	6,074	5,370	5,674
Weight of ELVs*	4,789	7,108	6,096	5,540	5,109	5,332	5,279	5,217	5,130	5,708	6,758	6,909	6,156	6,526

* Values multiplied by 1,000; The Eurostat estimates given for the period 2009–2011, 2013, and 2021.

End-of-life Vehicles

The decline in annual light vehicle sales in Europe, Japan, and North America between 2019 and 2022, amounting to a total reduction of 9.4 million units, combined with the global COVID-19 pandemic, significantly disrupted vehicle circulation in the market and, consequently, the supply chain for secondary raw materials [22].

From an environmental, technological, and economic perspective, the collection of ELVs is one of the first essential steps of the recycling of PGMs from spent ACCs [38]. In the period from 2008 to 2021, the total number of ELVs reported in the EU was over 78 million, corresponding to a total waste generation of over 76.3 million tonnes (Table 3). The total number of ELVs reported in the EU in 2021 was estimated at 5.674 million, which represents an increase of 5.7%, compared to 2020. Among the member states, the number of ELVs reported in the EU in the period 2008–2021 was the highest in Italy and France, followed by Spain and Germany [39].

According to Directive 2000/53/EC on ELVs [16], since 2015, the EU member states have had to introduce systems to meet the required recycling and reuse rates of at least 85% of the average weight per vehi-

cle and the recovery and reuse requirements of at least 95% for all new vehicles placed on the market [40]. In the context of ELVs, 'recycling' means any reprocessing of the waste materials, either for the original purpose or for other purposes, including backfilling operations (the use of non-hazardous materials resulting from dismantling or shredding for technical purposes) but excluding energy recovery, whereas 'recovery' is related to any process that can be categorised as recycling (including backfilling) or energy recovery [39]. During the period 2008–2014, the targets were lower and amounted to a recycling/reuse rate of 80% and a recovery/reuse rate of 85%. As shown in Figure 4, the overall recycling and recovery rates of ELVs were generally on an upward trend. In 2021, 20 of the EU member states reported recycling/reuse rates of ≥85%, with 4 states reporting rates in the range of 80.0–84.9%. In the same year, 18 states reported recovery/reuse rates of >95%, 3 countries each reported rates in the ranges of 90–94.9% and 80.8–85.8%.

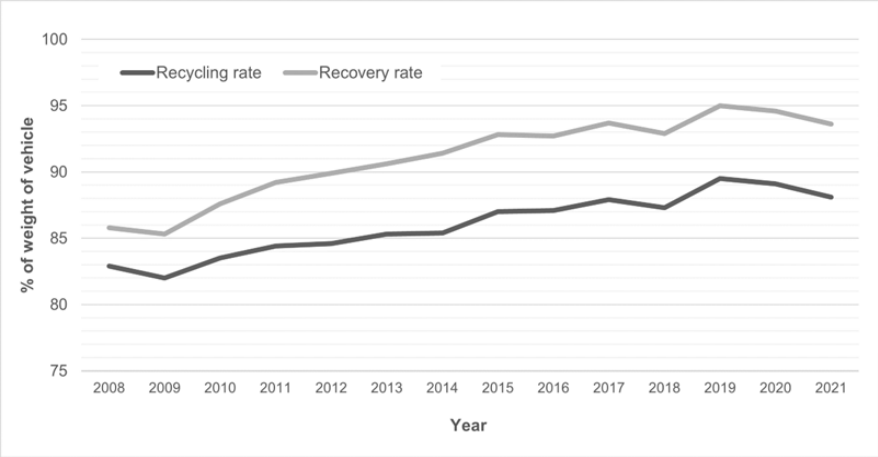


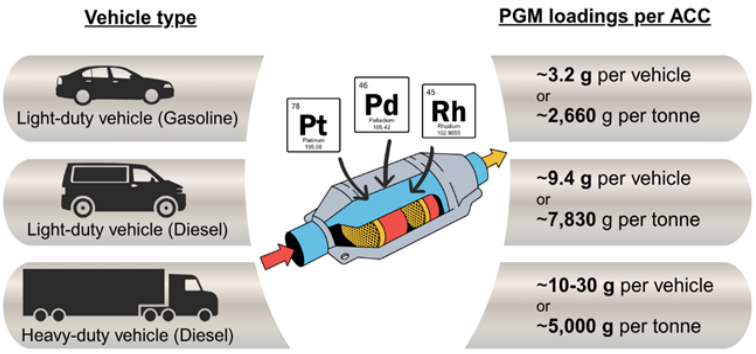
Figure 4. The total recycling and total recovery rates (%) of end-of-life vehicles in the European Union in the period 2008–2021 [39]

Automotive Catalytic Converters

The most common structure of an ACC is a honeycomb-type cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) skeleton with a density of 60–120 cells per cm^2, which is placed in a thermally insulated stainless steel box. To increase the contact area with gases, the skeleton is coated with a very porous wash coat (50–200 μm of thickness) consisting of 90% γ-Al_2O_3, and a mixture of base metal additives (mainly oxides of Ce, Zr, La, Ni, and Fe). As the active components of the ACCs, the PGMs are impregnated into the wash coat mainly in the form of salts of hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$), palladium(II) chloride ($PdCl_2$), and rhodium(III) chloride ($RhCl_3$) [2,4,30]. The Pt content in catalytic converters depends on the defined air pollution standard and the type and size of the vehicle engine (Figure 5a) [41]. For example, the Pt content ranges from 1–2 g in ACCs installed in smaller cars, meeting the less regulated emission standards, to 12–15 g Pt in larger trucks subject to stricter standards [32]. Pd and Rh could be present in ACCs in a wide range of 3.8–5,820 ppm and 1.1–2,390 ppm, respectively. The total PGMs loading could range from 140 ppm to 12,000 ppm per ACC [42], certainly much higher than the contents in the primary PGMs ores, and at the same time sustainably renewable compared to the projected mineral reserves (Figure 5b).

In general, the service lifetime of ACC is estimated to be more than 10 years of use [30], or 160,000 km for petrol vehicles and 200,000 km for diesel vehicles [3]. During use, converters can be deactivated due to fouling (usually caused by coke deposits), poisoning (occupation of active sites on the catalytic converter surface by catalytic reaction products), and/or degradation due to thermal shocks caused by numerous heating and cooling cycles of the converter [4]. It should also be mentioned that PGMs are thermally mobilised and mechanically ablated during the lifetime of converters, resulting in the emission of PGM-rich particles into the environment [43,44]. High concentrations of Pt, Pd, and Rh in different samples of soils and dust collected at sites adjacent to roads have been confirmed in many studies [43,45,46], thus presenting not only an environmental, but also an economic problem, since a certain quantity of the PGMs is lost. The highest recorded concentrations of Pd and Pt in the soil sampled up to 5 m from the edge of the expressway of urban and roadside environments of Toronto (Canada), amounting to 320 ppm and 128 ppm, respectively. Also, high concentrations of Pt, Pd, and Rh were detected in the street dust sampled at street shoulders of the expressway, amounting to 0.121 ppm, 0.026 ppm, and 0.0078 ppm, respectively [46]. For comparison, the average Pt concentration in soils without anthropogenic impact is approximately 0.14 ppb [43].

a)



b)

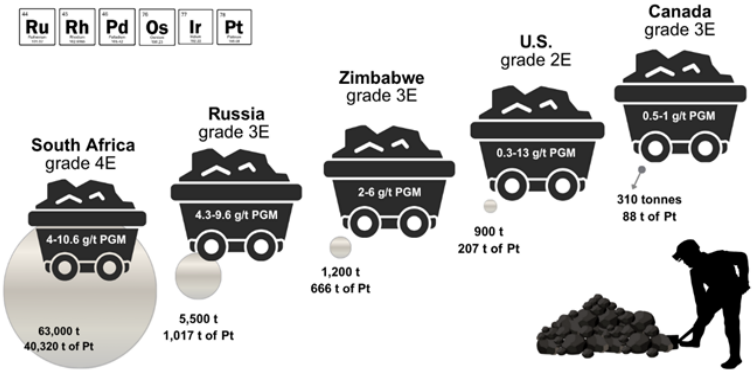


Figure 5. (a) The PGM loadings per spent automotive catalytic converters (grams) depending on the vehicle type used in secondary production of PGMs [30,32,41,42]; (b) The average contents of PGMs in ores (g t^{-1}) regarding the largest primary producers of PGM in the world and estimated reserves (tonnes) of a different grade (2E=Pt+Pd, 3E=Pt+Pd+Rh; 4E=Pt+Pd+Rh+Au) [47]

Table 4. The difference in environmental impact potential between primary and secondary production of PGMs per kg of metal [48]

Impact category	Platinum		Paladium		Rhodium		Iridium	Ruthenium
	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Primary
Global warming potential [kg CO_2 eq.]	36,828 18,333(1) 14,383(2)	477	28,094 18,179(1) 15,937(2)	497	38,027 18,612(1) 14,507(2)	497	42,096 19,456(1) 14,564(2)	42,000 19,486(1) 14,954(2)
Primary energy demand [MJ]	494,563	9,976	425,546	10,370	508,222	10,402	548,987	547,114
Acidification potential [mole of H^+ eq.]	1,687	1.26	4,507	1.29	1,446	1.30	887	926
Eutrofication potential [mole of N eq.]	687	3.68	450	3.70	715	3.77	812	811
Photochemical ozone creation potential [kg NMVOCs eq.]	258	0.95	380	0.95	249	0.97	236	238
Blue water consumption [kg]	297,006	2,419	343,960	3,654	305,879	3,458	335,220	329,931

NMVOCs – Non-methane volatile organic compounds; Blue water consumption – The amount of fresh water from surface or groundwater sources used for anthropogenic activities; (1) Conservative scenario for reduction of global warming potential modelled for 2030, reference year 2022; (2) Best-case scenario for reduction of global warming potential modelled for 2030, reference year 2022.

The LCA, which included in the analysis >95% of global primary (Russia, South Africa, U.S., and Zimbabwe) and about 60% of secondary (China, Germany, Japan, South Africa, UK, and U.S.) production of PGMs (Pt, Pd, Rh), showed that more than 98% of CO_2 eq. per kg of PGMs and 90% of energy consumption were reduced. The water consumption needed for recycling is less than 4 kg per kg of PGMs, compared to hundreds of kg of water used for primary production (Table 4). However, estimates are that from 35% to 61% of CO_2 eq. emissions from the primary production of PGMs will be reduced due to the shift from hard coal towards renewable energy sources in South Africa, depending on whether a conservative or best-case scenario is modelled for 2030, respectively [48].

Recycling of Spent Automotive Catalytic Converters

After deactivation, ACCs become valuable secondary materials. The economic sustainability of recycling is determined by a few crucial factors summarised at the microeconomic level (e.g. waste type and composition, current market prices for recyclable metals, revenues, energy utilization, environmental regulations, safety standards, etc.) and at the macroeconomic level (e.g. resource conservation, security of supply, responsible sourcing, reduced carbon footprint and supply effect on environment, reduced costs from landfilling or waste treatment, etc.). For efficient recycling, simply having a highly efficient process as the final step is not sufficient. Efficiency in retaining the high value of the process must be maintained throughout the entire recycling chain, from the collection of end-of-life products to pre-processing and final processing. A lower quality of the recycling process will result in higher metal losses. The overall efficiency is usually determined by the weakest link in the chain, which is often the collection process [49].

The recycling process of spent ACCs depends on three main factors: the loading of PGMs per converter, the properties of the PGM carriers and the wash-coat additives, and the load of impurities that have accumulated on the catalyst [50]. The combination of these factors represents a complex system containing a multicomponent base with a relatively low PGM content [51]. The methods used for the recycling of spent ACCs can be categorised into two main groups: hydro- and pyrometallurgy [4]. The main advantage of the pyrometallurgical method is the high recovery rate, but the high energy consumption is its disadvantage. Maximising the recovery of PGMs from spent ACCs is crucial for both environmental and economic reasons, often achieving recoveries of up to 93% for Rh and up to 97% for Pt and Pd. Melting the cordierite skeleton of converters requires high operating temperatures (1,500–1,900 °C), the addition of fluxes, and a long processing time in specialised equipment, making it unsuitable for small-scale facilities. In addition, rare earths such as Ce and Zr are also financially viable and cannot be recovered as they concentrate in the slag phase during concentrate processing [41,52]. The basic route of recovering PGMs from spent ACCs by hydrometallurgy involves five main steps: sampling/homogenization, pre-concentration, dissolution (*i.e.* leaching), metal isolation, and purification [30]. Subsequently, PGMs are usually collected from the leached solution by precipitation or cementation reactions or solvent extraction [50]. Gas-phase volatilisation or selective chlorination processes represent the third group of recycling methods that have several economic and environmental advantages over the metallurgical method, especially in the case of Rh recovery, since the hydrometallurgical method is considered economically unviable [53]. Suggested by Shen *et al.* [54], multi-combined processes could also be applied, consisting of pre-treatment of the crushed catalyst in the air at 800 ºC, followed by chlorination and leaching. In recent years, some new recycling methods have been considered, using a magneto-hydrodynamic (MHD) pump [38], in which cut monoliths are mechanically crushed to boost the reaction surface area after the liquid refined Pb is introduced into the channel of the MHD pump. The MHD pump consists of a driver made of magnetic cores on which the multiphase windings are wound and a channel for the liquid Pb between the cores. By rinsing the catalysts several times with Pb, the contained PGMs are transferred into the liquid phase. However, additional steps must be taken in order to extract the PGMs.

Ghodrat *et al.* [55] compared pyro- and hydrometallurgical methods of PGMs recovery using the Life Cycle Assessment (LCA). The results indicated that hydrometallurgy has a minor effect on the environment, in regard to the global warming effect, ozone layer depletion, eutrophication, and human health. Hydrometallurgy proved to be extremely beneficial in terms of lower operating temperatures, recovery of co-metals, easy control of process parameters, and it can be implemented in small-scale and large-scale facilities. In addition, the liquid effluent generated during leaching is simpler to control compared to the gaseous products released during pyrometallurgical processes [42]. Combined pyro/hydrometallurgical processes are in use, for instance, at the Umicore precious metal refinery in Belgium. Cu, Pt, and other metals from the mixture of spent ACCs and electronic waste are recovered by smelting, with the produced concentrate being further processed by hydrometallurgy [4]. Ivanović *et al.* [56] proposed a pyrometallurgical method combined with electrolytic refining for the treatment of spent ACCs in order to obtain high-purity Cu cathodes (99.99%) and PGMs (mainly Pt and Pd) of equal purity. In addition to the selection of the recycling method, the limitations associated with the application of recycled PGMs should also be considered. Andersson *et al*. [57] concluded that only Pt from recycled ACCs from ELVs can be functionally reused for the same application. The high recovery rates for PGMs are the focus of novel recovery methods, as well as cost effectiveness and eco-sustainability [58]. The selection of less toxic and less flammable extractants, such as ionic liquids,

for the recovery of PGMs from solution, offers advantages for hydrometallurgical processes in terms of higher recovery rates and safety of operating conditions [42]. Other than the Umicore plant, the recovery and refining of PGMs from secondary materials has already been successfully implemented in facilities such as Heraeus (Germany), BASF/Engelhard (U.S.), Johnson Matthey (United Kingdom), and Nippon/Mitsubishi (Japan) [30].

Table 5. Key differences between pyrometallurgical, hydrometallurgical, and bioleaching processes employed for the recovery of platinum-group metals from spent automotive catalytic converters

Parameter	Pyrometallurgical	Hydrometallurgical	Bioleaching
Energy consumption	High (>1,200–1,800 °C)	Low to moderate (<105 °C)	Low to moderate (25–80 °C)
Reagent use	Fluxes (cryolite, borax, lime, soda ash, etc.), base metal collectors (Fe, Cu, Ni, Pb), reductants (C, coke, etc.)	Strong acids and bases, oxidants, complexing agents, etc.	Microorganisms (bacteria, fungi, archaea) and enzymes; Acids.
Application	Large-scale facilities	Small- to medium-scale facilities	Small-scale facilities
Recovery rates*	High (>95%)	High for Pt and Pd (>95%), lower for Rh (<70% without pre-treatment)	Low to high, depending on the metal (>30–95%)
Co-metal recovery	Very limited	High selectivity (base metals, Ce, Zr)	High selectivity (base metals)
Main disadvantages	High environmental impact regarding emissions of waste gases, dust, and solid waste generation (slug); High flux consumption; Need of a large amount of waste input.	Chemically complex process; Emission of liquid effluents that need treatment; Emission of toxic gases; Corrosivity of used solvents and formed products.	Extensive PGM extraction methodology; Slow kinetics; Lower recovery rates; Not commercialised method.
Main advantages	High recovery rates of PGMs (>95–99%); High capital investment for equipment and infrastructure; Continuous, well-established industrial process; Fast process; Possibility of melting other scrap materials (e.g., electronic waste) in the same batch.	Lesser capital investment compared to pyrometallurgy; Moderate impact on the environment; Highly controllable process; Replacement of strong acids with eco-friendly reagents.	Low-cost method; Use of more eco-friendly Solvents compared to hydrometallurgy; The most sustainable recovery process; Economical technology.

* The recovery rates for PGMs are generalised.

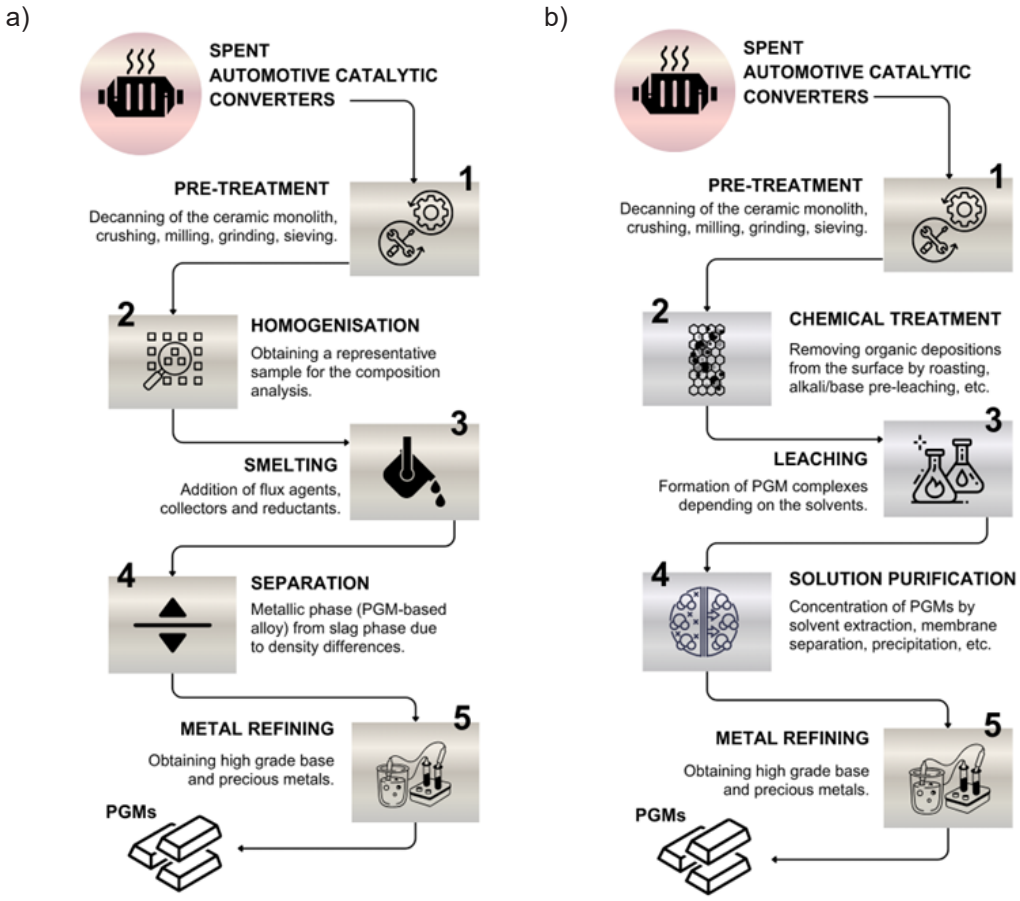


Figure 6. Simplified flow diagrams of the main steps regarding (a) pyrometallurgical and (b) hydrometallurgical routes for recovering PGMs from spent automotive catalytic converters

Prior to recycling, ACCs need to be well prepared and homogenised to obtain a representative sample for the composition analysis, as the content of PGMs and base metals significantly influences the selection of the recycling method that ensures high recovery rates [30]. Regardless of the method, the processing of ACCs initially involves de-canning of the ceramic monolith. In the pyrometallurgical route, the waste material is placed in a smelter with fluxes and collector metals, while in the hydrometallurgical route, the material undergoes pre-treatment, including residue cleaning. In order to remove Fe-containing impurities that may originate from the de-canning phase, magnetic separation can be applied [42]. Thermal pre-treatment prior to leaching is often suggested, e.g., pre-treatment in a hydrogen stream (at a temperature of 250 °C), in an air stream (250 °C) [2], or in a Zn vapour stream (>600 °C) [59]. For example, the hydrogen stream stabilises the PGMs in their metallic form, while at higher temperatures, adhered C_nH_m and charcoal from the catalyst surface are eliminated [2]. In addition to thermal pre-treatment, grinding and calcination can also be used. The results of the study by Sun *et al.* [60] showed that of three different pre-treatment methods, such as grinding, calcination, and reduction, grinding reduced the leaching rate of PGMs, while reduction with HCOOH and calcination with $NaHSO_4$ improved the leaching of Pt and Rh, respectively.

Table 5 summarises the data on the key performance indicators of the different processes for the recovery of PGMs from spent ACCs, while in Figure 6 the main steps of pyrometallurgical (Figure 6a) and hydrometallurgical (Figure 6b) processes are compared.

Solutions for PGMs Leaching from Spent ACCs

Based on the oxidising agent, the leaching of Pt and other precious metals can be performed by leaching: with aqua regia (after pre-treatment), in the presence of chloride ions, with hydrogen peroxide, with cyanides, with iodide/iodine, and other solutions [4]. *Aqua regia* is considered to be one of the most effective leaching agents for PGMs, capable of completely dissolving both Pt and Pd from ACCs. However, due to the significant challenges in practical application associated with high handling costs and environmental concerns, such as the generation of toxic and corrosive NO_x gases and acid fumes that require chemical treatment and cause failure of the equipment [2,4,60], aqua regia has become a less competitive leaching agent. The high concentrations of HCl can only partially dissolve PGMs, and oxidants other than HNO_3, such as H_2O_2, Cl_2, and $NaClO_3$, need to be added. The specific reactions of the two most commonly used oxidants, H_2O_2 and HNO_3, with Pt, Pd, and Rh are given in Eqs. (1)-(10) [3,30,60]:

$$PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^-;\ E_0 = 0.74\ V \quad (1)$$

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^-;\ E_0 = 0.73\ V \quad (2)$$

$$PdCl_4^{2-} + 2e^- \rightarrow Pd + 4Cl^-;\ E_0 = 0.62\ V \quad (3)$$

$$RhCl_6^{3-} + 3e^- \rightarrow Rh + 6Cl^-;\ E_0 = 0.44\ V \quad (4)$$

$$Pt + 6HCl + 2H_2O_2 \rightarrow PtCl_6^{2-} + 2H^+ + 4H_2O \quad (5)$$

$$Pd + 4HCl + H_2O_2 \rightarrow PdCl_4^{2-} + 2H^+ + 2H_2O \quad (6)$$

$$Rh + 12HCl + 3H_2O_2 \rightarrow 2RhCl_6^{3-} + 6H^+ + 6H_2O \quad (7)$$

$$3Pt + 18HCl + 4HNO_3 \rightarrow 3PtCl_6^{2-} + 6H^+ + 4NO + 8H_2O \quad (8)$$

$$3Pd + 12HCl + 2HNO_3 \rightarrow 3PdCl_4^{2-} + 6H^+ + 2NO + 4H_2O \quad (9)$$

$$Rh + 6HCl + HNO_3 \rightarrow RhCl_6^{3-} + 3H^+ + NO + 2H_2O \quad (10)$$

In industrial practice, the method of wet chlorination in the presence of HCl acid for the recovery of precious metals is also not widely used as chlorine is a highly corrosive, toxic, and dangerous gas. Particularly, handling, using, and disposing of excess chlorine are challenging and difficult tasks of the method. However, Kim *et al.* [5] proposed an eco-friendly treatment technique of in-situ electro-generated chlorine, compared to the conventional treatment process of chlorination. In the cathodic compartment of an in-situ cell for chlorine electro-generation, the undamaging treatment was accomplished through the electrochemical reduction of unconsumed gas [5]. This would markedly decrease the requirements for chlorine supply and enhance the overall safety of the process. Regarding the amount of used chlorine, it could be reduced by carbochlorination by introducing CO into the gas mixture, according to Kim *et al.* [53].

Hammadi *et al.* [63] studied the optimal conditions for leaching Pt and Pd from the powder sample (<250 μm) of catalytic converters with aqua regia solution for three operating factors: time (30–120 min), temperature (25–100 °C), and solid to liquid ratio (S/L 1:5–1:20). The experiments showed that the increase in the level of each factor tended to increase the leaching efficiency of Pt and Pd, resulting in the following optimum conditions: 120 min, 100 °C and S/L ratio of 1:20. At these conditions, the resulting leaching efficiencies were >97% for Pt, and >93% for Pd. After the leaching, Pt was initially precipitated as $(NH_4)_2PtCl_6$ by adding 5 mol L^{-1} NH_4Cl, while Pd was precipitated in the form of $(NH_4)_2PdClO_3$ from the remaining solution by adding 5 g L^{-1} $NaClO_3$. After the precipitation step, which was performed at 50 °C for 1 h, the total recoveries of Pt and Pd were 91.94% and 98.82%, respectively. The leaching of Pd, Pt, Rh, and Ru in a microwave with the Cloud Point Extraction (CPE) proves to be a fast and efficient method considering the energy use, according to Suoranta *et al.* [64]. The leaching efficiencies of pulverised spent monolith automotive catalysts (<74 μm) were compared for three reagents, $HCl_{(conc.)}$, $HNO_{3(conc.)}$, and *aqua regia* in the temperature range of 90–210 °C. During CPE, PGM ions in reaction with a complexing agent formed neutral hydrophobic

complexes, which were extracted from an aqueous solution by adding a surfactant to micelles. Afterwards, by heating the system above its cloud point temperature, the phase loaded with surfactant was separated from the aqueous phase. A series of leaching experiments showed that concentrated HCl and aqua regia were able to leach more than 90% of Pd, Pt, Rh, and Ru at >150 °C, while slightly lower leaching gains were observed at 120 °C (78–93% of Pd, Pt, Rh, and Ru). Suoranta *et al.* [54] studied diluted HCl (1 mol L^{-1}), considered a relatively environmentally friendly leaching reagent, where the recoveries obtained were 91±6% for Pd, 91±5% for Pt, 85±6% for Rh, and 66±11% for Ru, at 120 °C. As for the amount of matrix elements (Al, Ce, Zr) in the ACCs, the content was also reduced by over 95% during CPE. Sun *et al.* [60] reported an environmentally friendly route for leaching spent ACCs, but with lower outcomes. After calcination pre-treatment of the samples with Li_2CO_3, the achieved leaching efficiencies of Pt, Pd, and Rh were 70.87%, 55.48% and 27.12%, respectively, under optimal conditions of 12 mol L^{-1} HCl for 2 h at 80 °C.

According to the Eh-pH diagrams, the dissolution of Pt, Pd, and Rh in binary mixtures of HNO3/HCl and H_2O_2/HCl is thermodynamically possible (Eqs. (1)-(4)), which is important since the usage of less harmful leaching reagents is environmentally beneficial and sustainable [2]. De Aberasturi *et al.* [2] confirmed that more than 95% of the recovery rate could be obtained by replacing HNO3 in *aqua regia* with H_2O_2. The proposed mixed reagent contained 80 mL of HCl (12 mol L^{-1}), 5 mL of H_2O_2 (110 vol.), and 5 mL of H_2SO_4 (18 mol L^{-1}). The energy consumption for the leaching process was studied at the optimum temperatures (65 and 90 ºC) and for different reaction times (2, 4, 6, 8, and 10 h). The results showed that the extraction rates for Pt, Pd, and Rh increased at 90 ºC as the reaction time increased to 6 h. For better leaching results, thermal pre-treatment at 250 ºC for 22 h was applied. Quantitative solvent extraction of PGMs was also studied by D'yachkova *et al.* [51], by autoclave decomposition of ACCs in the temperature range of 160–240 °C for 0.5–4 h, using binary mixtures of HCl/HNO3 and HCl/H_2O_2. Under the optimum conditions (temperature 220 °C, decomposition time 1.5 h, sample weight 0.5–1.0 g, and reagent volume 10 mL), the leaching results for Pt, Pd, and Rh differed slightly (0.03% to 0.30%) between the two binary mixtures. Rumpold and Antrekowitsch [52] showed that, in addition to the PGMs, Ce can also be recovered from spent catalysts with a mixed HCl/H_2O_2 leaching agent, with a recovery rate of 86%. By adding precipitation agents (potassium and sodium sulphate, and H_2SO_4), insoluble $Ce(SO_4)_2$ is formed. Aluminium was used as a suitable agent for cementation, resulting in the recovery of 90% of Pt and 65% of Rh. The authors proposed the regeneration of the leaching solution, which minimises wastewater generation, while the process residues represent potential by-products for the refractory industry and paper production. Atia and Spooren [65] showed a new, extremely fast microwave-assisted leaching process in 6 mol L^{-1} HCl to solubilise Pt, Rh, and Ce from ACCs. Leaching was conducted without milling (the honeycomb structure was retained after leaching), oxidation agents, and internal mixing (which simplified the reactor design), resulting in lower overall process costs. The highest extraction yields were 99±4% of Pt, 95±1% of Rh, and 104±3% of Ce, at a temperature of 220 °C, and a liquid to solid ratio of 1:10 for 3 min in the microwave. In addition, the authors proposed a sustainable PGMs extraction by reducing the amount of HCl for extraction by adding 3.8 M NaCl under the same operating conditions, which resulted in a reduction of the overall recovery, yielding a leaching efficiency of 68±2% Pt and 67±5% of Rh. The results also showed a lower solubilisation of Ce (39±1%). Nogueira *et al.* [66] showed an effective leaching process for the recovery of Pd and Rh from spent ACCs using Cu^{2+} ions as a suitable oxidising agent for PGMs at high Cl^- concentrations. The suitability of the aqueous HCl/Cu^{2+} leaching media, as an alternative reactant system to the conventional ones, was proven, as the maximum recoveries of 95% Pt and 86% Pd were achieved under optimised conditions (80 ºC, 4 h, 6 mol L^{-1} HCl, 0.3 mol L^{-1} Cu^{2+}). According to the experimental data, the most important parameters for the leaching of Pt and Pd were the concentrations of HCl and Cu^{2+} ions, as well as the temperature in the case of Rh. The effect of leaching time was significant for Rh, as the maximum recovery yield was reached after 4 h of reaction time, while the maximum leaching rate for Pt was reached after 1 h.

The advantages of cyanides over acids are related to lower corrosion, the possibility of selective PGMs extraction, lower base metal dissolution, no need for chemical transport, etc. On the other hand, the excessive use of cyanide is associated with higher environmental risks. In this regard, biological cyanidation is considered to be one of the highly promising, eco-friendly methods, as bacteria produce cyanide and can subsequently detoxify it [67]. Chen and Huang [28] proposed a two-stage pressure cyanidation method in a 50 L autoclave, as the chemical reaction between NaCN and PGMs is kinetically weak at room temperature and atmospheric pressure. The pre-treatment by pressure alkaline leaching (160 °C, 25 g L^{-1} NaOH, 2 h, $p(O_2)$ = 2 MPa, L/S ratio of 4:1) was applied in order to remove carbon and gasoline impurities accumulated on the surface of ACCs. The optimum conditions for the two-stage cyanidation in a 5 kg-scale batch experiment were: 160 °C, 6.25 g L^{-1} NaCN, 1 h, $p(O_2)$ = 1.5 MPa, L/S ratio of 4:1, with the obtained recoveries of Pt, Pd and Rh being 95–96%, 97–98% and 90–92%, respectively, by zinc cementation (60–80 °C, pH 9.5–10, 2 h, 1 atm). During the proposed method of pressure cyanide leaching of PGMs, the following chemical reactions (Eqs. (11)-(16)) occurred [28,30,68]:

$$2Pt + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2[Pt(CN)_4] + 4NaOH \quad \text{.....(11)}$$

$$2Pd + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2[Pd(CN)_4] + 4NaOH \quad \text{.....(12)}$$

$$2Ph + 24NaCN + 3O_2 + 6H_2O \rightarrow 4Na_3[Ph(CN)_6] + 12NaOH \quad (13)$$

$$Pt(CN)_4^{2-} + \frac{3}{2}O_2 + 7H_2O \rightarrow Pt + 4NH_3 + 4CO_2 + 2OH^- \quad (14)$$

$$Pd(CN)_4^{2-} + \frac{3}{2}O_2 + 7H_2O \rightarrow Pd + 4NH_3 + 4CO_2 + 2OH^- \quad (15)$$

$$Rh(CN)_6^{3-} + \frac{9}{4}O_2 + \frac{21}{2}H_2O \rightarrow Rh + 6NH_3 + 6CO_2 + 3OH^- \quad (16)$$

Due to the bonding strength of the PGMs, Chen and Huang [28] noted the order of cyanide leaching efficiencies as Pt>Pd>Rh.

A two-stage process was developed by Shin *et al.* [67] in order to improve biological cyanidation leaching, such as low production of cyanide and an unsuitable pH needed for bacterial growth. The results showed that biogenic cyanide can replace chemicals for the leaching of the PGMs from spent ACCs. In the first stage, cyanide was produced biologically by the cyanide-producing bacteria *Chromobacterium violaceum* and then used in a separate vessel to recover PGMs in the second stage of the process. Under the same conditions ($[CN^-]$ = 1,000 mg L^{-1}, 150 °C, 1 h, 200 rpm), the leaching efficiencies of Pt, Pd and Rh with biogenic cyanide were 92.1%, 99.5% and 96.5%, respectively, which were slightly lower compared to the leaching efficiencies with chemical cyanide (100%, 99.9% and 100%, respectively). Due to the high chemical inertness of Rh, lower recovery rates for Rh leaching are noted in the literature [58]. However, Shin *et al.* [67] have shown that biogenic cyanide can leach Rh in high percentages.

Solvometallurgy is a new extractive metallurgy concept that aims at metal recovery using nonaqueous solutions. This approach can be utilised for the selective leaching of metals, taking advantage of the differences in mechanisms of metal extraction. Solvometallurgy complements pyrometallurgy and hydrometallurgy, offering several benefits: minimal water consumption with no wastewater generation, combined leaching and solvent extraction in one step for simplified processes, and higher selectivity compared to acidic leaching [69]. Organic extractants have also proven to be efficient in combination with chloride or other solutions. Lee *et al.* [70] developed a complete solvent extraction route at a laboratory scale for the separation and recovery of Pd and Pt from chloride leach liquors by commercial organophosphorous and amine-based extractants at room temperature (30±1 °C) and distilled kerosine (96.2%) as diluent. The proposed method could be applied for PGMs extraction from spent ACCs. The used extractants for Pd and Pt were tri-n-butyl phosphate (TBP) and quaternary amine Aliquat 336, respectively. The quantitative and selective separation of Pd from Pt and other base metals (Cr, Mn, Ni and Fe) was carried out by extraction with 0.0054 mol L^{-1} TBP in two stages at an aqueous to organic phase (A/O) ratio of 3.75, after which the stripping of Pd from the loaded organic phase was conducted by 0.5 mol L^{-1} thiourea (O/A ratio of 5) at low HCl concentration (0.1 mol L^{-1}), corresponding to a Pd extraction efficiency of 99.9%. On the other hand, for Pt extraction required 0.011 mol L^{-1} Aliguat 336 at an A/O ratio of 3, while the stripping solution contained 0.5 mol L^{-1} thiourea (O/A ratio of 4) at a low acid concentration (0.5 mol L^{-1} HCl), corresponding to a Pt extraction efficiency of 99.83%. Nguyen *et al.* [71] studied the leaching of PGMs from spent ACCs using two oxidising agents, $FeCl_3$ or $CuCl_2$, in organic solvents, dimethyl sulfoxide (DMSO) or acetonitrile (CH_3CN). The oxidative dissolution of Pt, Pd, and Rh depended on the temperature, leaching time, concentration of oxidizing agent, and S/L ratio. Pd was quantitatively dissolved with 0.01 mol L^{-1} $FeCl_3/CH_3CN$, followed by complete leaching of Pt and Rh with 0.3 mol L^{-1} $FeCl_3/CH_3CN$. The solvent CH_3CN was recovered by distillation after both selective leaching. In order to separate Fe and Pt from Rh in ethylene glycol, the nonaqueous solvent extraction using Aliquat 336 (ionic liquid diluted in the green solvent *p*-cymene) was employed. Subsequently, the recovery of Fe and Pt from the ionic liquid phase and the regeneration were done by selective stripping with water and a thiourea solution, respectively.

Reddy *et al.* [72] have also studied the solvent extraction method of selective separation and complete recovery of Pd from the leach liquor with extractant 0.5 vol.% LIX 84I (2-hydroxy-5-nonylacetophenone oxime in a mixture with a high flash point hydrocarbon diluent) in kerosene. After the extraction of Pd at an A/O ratio of 3, in two stages, stripping from the loaded organic was achieved with acidified (0.5 mol L^{-1} HCl) thiourea at a low concentration of 0.5 mol L^{-1}. The quantitative co-extraction of Fe and Pt was possible from the raffinate, with 5 vol.% Alamine 336 (tertiary amine of mixed tri-octyl/decyl amine) in kerosene, at an A/O of 2. Selective scrubbing of Fe was done in two stages (dilute HCl, A/O of 1.5), after stripping of Pt from the loaded organic was achieved with 0.1 mol L^{-1} HCl and 0.5 mol L^{-1} thiourea at an A/O of 4. The purity of the obtained Pd and Pt strip solutions was high, amounting to 99.7%.

Senthil *et al.* [73] suggested a very efficient method for the extraction of Pd from mixed metal/spent ACCs residues using the macrocyclic ligand MADTTCA (11,17,23-tetrakis-[(p-methoxyphenyl)azo]-25,26,27,28-tetrakis[(dimethyl thiocarbamoyl)oxy]thiacalix[4]arene) in an HCl acid medium, and chloroform as a diluent. The results showed that the synthesised reagent is a suitable candidate for industrial-scale application. The equilibrium extraction for Pd was achieved after an optimal contact time of 15 min with 0.1 mol L^{-1} thiourea in 1.0 mol L^{-1} HCl solution, with very high selectivity towards Pd (>99.7%), from a mixed solution of Pt, Rh, Al, La, and Ce ions. The following stripping reagents were discarded due to their low efficiency 0.1 mol L^{-1} HCl (only 7.8% Pd was stripped), 1.0 mol L^{-1} H_2SO_4 (4.3% Pd), 1.0 mol L^{-1} HNO_3 (22.7% Pd), and 2.0 mol L^{-1} acetic acid (8.6% Pd). In addition to the sustainability of the method, the proposed extractant could be reused at least 5 times without any significant loss of its properties. The maximum loading capacity of Pd was found to be 417 mg L^{-1} using 1.0

mmol L^{-1} MADTTCA at the stoichiometric ratio of 1:1.

Ilyas *et al.* [74] showed the results of liquid–liquid separation of Pt, Pd, and Rh from a chloride leach solution applying the Cyphos IL 101, which is a phosphonium-based ionic liquid. After 30 min at an O/A ratio of 1, the achieved leaching extraction for Pt and Pd was 99%, while the efficiency for Rh was significantly lower at 22%. Since Rh can affect the purity of Pt and Pd, it was imperative to efficiently scrub out Rh from the loaded ionic liquid. The concentration of the 5.0 mol L^{-1} HCl solution was optimised for scrubbing >93% of Rh. Subsequently, Pt was quantitatively stripped over Pd with 0.1 mol L^{-1} NaSCN solution in two stages of counter-current with an efficiency of ~99%, leaving Pd in the Pt-depleted organic phase from which it was stripped in a single stage of contact with 0.02 mol L^{-1} CH_4N_2S solution, resulting in >99% Pd recovery. The results of the extraction-stripping cycles clearly demonstrated the stability and reusability of the proposed ionic liquid as a potential green extractant with excellent regeneration performance while maintaining the constant leaching efficiency after five cycles of regeneration.

Conclusion

It is evident that the current approach of utilising valuable materials of secondary origin must be changed for both economic and environmental reasons. Recycling is preferable and highly beneficial for end-of-life products, such as spent automotive catalytic converters that contain various economically recoverable metals (including platinum-group) and materials, enabling their economical reuse. Regarding PGMs, the use of virgin raw materials, which have a significant environmental impact during mining and processing of PGM-containing ores, needs to be avoided, and as a premise of sustainable development, the recycling of PGMs from secondary raw materials should be prioritised. The integration of circular economy concepts into the PGM recovery will provide significant opportunities for sustainability through improved recycling methods. Recycling of spent ACCs can reduce the carbon footprint and overall environmental impact of raw material processing and prevent the generation of waste as much as possible by lowering the need for landfilling, minimising the risk of emission of hazardous and harmful substances into air, water, and soil as well. The high and repeatable recyclability of PGMs lowers the environmental impact with each cycle, reducing the overall environmental footprint of secondary production. Recycling of ACCs can significantly increase the supply security for critical raw materials, such as PGMs. In addition to the production of catalysts for the automotive industry, PGMs play an important role in green technologies, making them strategic raw materials of global importance. PGMs are particularly needed in the ongoing energy transition, such as the decarbonisation process of the transport sector, and the improvement and development of fuel cell technologies.

However, the continuing global demand for PGMs cannot be met from the primary sources but must rely on recycling. Regeneration, reactivation, and reuse of spent automotive catalytic converters are also advisable, but ultimately, converters must be recycled. The recycling of spent automotive converters should be carried out in compliance with the highest environmental requirements and standards regarding all the steps of the recycling process, as catalytic converters are both harmful and valuable solid waste.

From an industrial perspective, pyrometallurgy is the predominant recovery technique, followed by hydrometallurgy, while biometallurgy is currently applied mostly on a laboratory scale. Since the smelting of PGM concentrates is limited by major challenges, mostly high energy consumption and environmental pollution, researchers have focused primarily on the development of advantageous and innovative hydrometallurgy methods. Leaching has become a preferred method for recovering PGMs due to its numerous advantages, including cost-effectiveness and environmentally friendly practices. Leaching technologies have demonstrated significant advantages over conventional pyrometallurgical methods, including lower operating temperatures, reduced use of hazardous reagents, the potential for simultaneous recovery of PGMs and co-metals such as Ce and Zr, improved control over operational parameters, scalability across different production capacities, and the generation of liquid effluents that are generally easier to manage compared to the gaseous emissions and solid residues characteristic of high-temperature pyrometallurgical treatments. However, due to the high chemical inertness of Rh, its lower recovery rates compared to Pt and Pd remain one of the issues that need to be improved, as well as the recovery of other valuable components from the wash coat of spent automotive catalytic converters, and the efficient utilisation of the by-products (e.g. SiO_2, Al_2O_3, and MgO).

In the coming years, the development of a viable supply strategy for spent automotive converters from end-of-life vehicles, together with the improvement and optimisation of the recycling process and the development of efficient large-scale facilities, will have a significant impact on the growth of the sustainable recycling industry, including waste reduction, lower consumption of water and energy, introduction of environmentally friendly reagents, repeatability, etc. Still, the current low collection rate of spent automotive catalytic converters, as well as the resale of older vehicles in countries with lower GDP that lack an organised system for collecting spent converters, lowers the overall efficiency and economical recovery of PGMs. Global geopolitical disturbances leading to economic uncertainty could further slow automobile sales and ultimately reduce automotive scrap volumes. Additionally, the shift to electric vehicles is expected to reduce global demand for PGMs, weakening the current recycling system for catalytic converters from end-of-life vehicles, and therefore redirecting attention toward alternative secondary raw materials in the future.

Furthermore, the EU is focused on achieving zero-CO_2 emissions for all new cars produced starting in 2035, leading to high demand for PGMs for at least the next decade. However, by focusing on innovative technologies and sustainable strategies, it is possible to reduce the global environmental impact of producing PGMs from secondary resources while meeting the demand for these critical and strategic metals in everyday use.

List of Symbols and Abbreviations

ELVs – End-of-life vehicles
PGMs – Platinum group of metals
ACCs – Automotive catalytic converters
TWCs – Three-way catalysts
CRMs – Critical raw materials
SRMs – Strategic raw materials
U.S. – The United States of America
EC – The European Commission
EU – The European Union
UK – The United Kingdom
2E – The grade of PGM ore, the sum of Pt and Pd
3E – The grade of PGM ore, the sum of Pt, Pd and Au
4E – The grade of PGM ore, the sum of Pt, Pd, Rh and Au
6E – The grade of PGM ore, the sum of Pt, Pd, Rh, Ru/Os, Ir and Au
CO_2 eq. – Equivalent mass of carbon dioxide
MDH – Magneto-hydrodynamic pump
LCA – Life Cycle Assessment
CPE – Cloud Point Extraction
L/S – Liquid to solid ratio
TBP – Tri-n-butyl phosphate
DMSO – Dimethyl sulfoxide
A/O – Aqueous to organic phase ratio

Acknowledgements

The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for financial support, within the funding of the scientific research at the University of Belgrade, Technical Faculty in Bor (Contract No. 451-03-137/2025-03/200131).

References

[1] Heck RM, Farrauto RJ. Automobile exhaust catalysts. *Applied Catalysis A: General.* 2001, 221, 443-457. https://doi.org/10.1016/S0926-860X(01)00818-3
[2] de Aberasturi JD, Pinedo R, de Larramendi IR, Ruiz de Larramendi JI, Rojo T. Recovery by hydrometallurgical extraction of the platinum-group metals from car catalytic converters. *Minerals Engineering.* 2011, 24, 505-513. https://doi.org/10.1016/j.mineng.2010.12.009
[3] Saurat M, Bringezu S. Platinum group metal flows of Europe, Part 1 - Global supply, use in industry, and shifting of environmental impacts. *Journal of Industrial Ecology.* 2008, 12(5/6), 754-767. https://doi.org/10.1111/j.1530-9290.2008.00087.x
[4] Jha MK, Lee J-C, Kim M-S, Jeong J, Kim B-S, Kumar V. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: A review. *Hydrometallurgy*. 2013, 133, 23-32. https://doi.org/10.1016/j.hydromet.2012.11.012
[5] Kim M, Park S, Lee J, Choubey PK. A novel zero emission concept for electrogenerated chlorine leaching and its application to extraction of platinum group metals from spent automotive catalyst. *Hydrometallurgy.* 2016, 159, 19-27. https://doi.org/10.1016/j.hydromet.2015.10.030
[6] Sverdrup HU, Ragnarsdottir KV. A system dynamics model for platinum group metal supply, market price, depletion of extractable amounts, ore grade, recycling and stocks-in-use. *Resources, Conservation and Recycling.* 2016, 114, 130-152. https://doi.org/10.1016/j.resconrec.2016.07.011
[7] Fernandez V. Some facts on the platinum-group elements. *International Review of Financial Analysis.* 2017, 52, 333-347. https://doi.org/10.1016/j.irfa.2017.04.003
[8] The PGM yearly market report, Johnson Matthey, May 2024. https://matthey.com/documents/161599/509428/PGM-Market-Report-24.pdf. Accessed March 3, 2025.
[9] Shen Y, Moomy R, Eggert RG. China's public policies toward rare earths, 1975–2018. *Mineral Economics.* 2020, 33, 127-151. https://doi.org/10.1007/s13563-019-00214-2
[10] Five lists of Critical Raw Materials. https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en. Accessed March 3, 2025.
[11] The first list of Critical Raw Materials, Communication from the Commission to the European Parliament, The Council, The European Economic and Social Committee and the Committee of The Regions, Tackling the Challenges in Commodity Markets and on Raw Materials, Brussels. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52011DC0025. Accessed March 3, 2025.
[12] The fifth list of Critical Raw Materials, European Commission, Study on the Critical Raw Materials for the EU 2023, Final Report, ISBN:978-92-68-00414-2. https://op.europa.eu/en/publication-detail/-/publication/57318397-fdd4-11ed-a05c-01aa75ed71a1. Accessed March 3, 2025.
[13] Metals for Clean Energy – Pathways to solving Europe's raw materials challenge. https://eurometaux.eu/media/rqocjybv/metals-for-clean-energy-final.pdf. Accessed March 3, 2025.
[14] America's Strategy to Secure the Supply Chain for a Robust Clean Energy Transition, U.S. Department of Energy Response to Executive Order 14017. https://www.energy.gov/policy/articles/americas-strategy-secure-supply-chain-robust-clean-energy-transition. Accessed March 3, 2025.
[15] Circular economy: Improving design and end-of-life management of cars for more resource-efficient automotive sector, European Commission. https://ec.europa.eu/commission/presscorner/detail/en/ip_23_3819. Accessed March 3, 2025.
[16] Directive 2000/53/EC of the European Parliament and of the Council on end-of-life vehicles, 18 September 2000, European Parliament, Council of the European Union, 02000L0053–EN–30.03.2023–015.001–2. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02000L0053-20230330. Accessed March 3, 2025.
[17] Communication from the Commission to the European

Parliament, The Council, The European Economic and Social Committee and the Committee of the Regions, A new Circular Economy Action Plan for a cleaner and more competitive Europe, Brussels. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0098. Accessed March 3, 2025.
[18] Zero waste, Whitepaper: Reimagining the Waste Framework Directive An EU Regulatory Framework for a Circular Economy consistent with 1.5 degrees, Eunomia, 2023. https://circulareconomy.europa.eu/platform/sites/default/files/2023-04/Reimagining-the-Waste-Framework-Directive-18-April-2023.pdf. Accessed March 3, 2025.
[19] United Nations, Transforming our World: The 2030 Agenda for Sustainable Development, A/RES/70/1, Department of Economic and Social Affairs Sustainable Development, 2015. https://sdgs.un.org/sites/default/files/publications/21252030%20Agenda%20for%20Sustainable%20Development%20web.pdf. Accessed June 17, 2025.
[20] Internal Market, Industry, Entrepreneurship and SMEs, Critical raw materials, European Commission. https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en. Accessed June 20, 2025.
[21] Study on the EU's list of Critical Raw Materials (2023) – Final Report, European Commission, Publications Office of the European Union. doi:10.2873/725585. https://op.europa.eu/en/publication-detail/-/publication/57318397-fdd4-11ed-a05c-01aa75ed71a1. Accessed June 20, 2025.
[22] The PGM yearly market report, Johnson Matthey, May 2025. https://matthey.com/products-and-markets/pgms-and-circularity/pgm-markets/pgm-market-reports. Accessed June 20, 2025.
[23] International Platinum Group Metals Association (IPA), The environmental profile of platinum group metals (PGMs), A cradle-to-gate life cycle assessment of the production of PGMs and the benefits of their use in a selected application, Reference Year 2017–2022 Update. https://ipa-news.de/assets/pdfs/2022-06-21-new-environmental-profile-of-pgms-ipa.pdf. Accessed June 17, 2025.
[24] The PGM yearly market report, Johnson Matthey, May 2023. https://matthey.com/johnson-matthey-publishes-latest-pgm-market-report-2023. Accessed March 3, 2025.
[25] The base price of PGMs, ©Johnson Matthey's 2024. https://matthey.com/products-and-markets/pgms-and-circularity/pgm-management. Accessed March 3, 2025.
[26] Gleich B, Achzet B, Mayer H, Rathgeber A. An empirical approach to determine specific weights of driving factors for the price of commodities – A contribution to the measurement of the economic scarcity of minerals and metals. *Resources Policy.* 2013, 38, 350-362. https://doi.org/10.1016/j.resourpol.2013.03.011
[27] Ravindra K, Bencs L, Van Grieken R. Platinum group elements in the environment and their health risk – Review. *The Science of the Total Environment.* 2004, 318, 1-43. https://doi.org/10.1016/S0048-9697(03)00372-3
[28] Chen J, Huang K. A new technique for extraction of platinum group metals by pressure cyanidation, *Hydrometallurgy.* 2006, 82, 164-171. https://doi.org/10.1016/j.hydromet.2006.03.041
[29] Mudd G.M. Key trends in the resource sustainability of platinum group elements, *Ore Geology Reviews*. 2012, 46, 106-117. https://doi.org/10.1016/j.oregeorev.2012.02.005
[30] Dong H, Zhao J, Chen J, Wu Y, Li B. Recovery of platinum group metals from spent catalysts: A review. *International Journal of Mineral Processing*. 2015, 145, 108-113. https://doi.org/10.1016/j.minpro.2015.06.009
[31] Mpinga CN, Eksteen JJ, Aldrich C, Dyer L. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. *Minerals Engineering.* 2015, 78, 93-113. https://doi.org/10.1016/j.mineng.2015.04.015
[32] Yang CJ. An impending platinum crisis and its implications for the future of the automobile. *Energy Policy*. 2009, 37, 1805-1808. https://doi.org/10.1016/j.enpol.2009.01.019
[33] Wilburn DR. Global exploration and production capacity for platinum-group metals from 1995 through 2015, U.S. *Geological Survey Scientific Investigations Report*. https://pubs.usgs.gov/sir/2012/5164/pdf/sir2012-5164_v1-1.pdf. Accessed March 4, 2025.
[34] Gibson BAKK, Nwaila G, Manzi M, Ghorbani Y, Ndlovu S, Petersen J. The valorisation of platinum group metals from flotation tailings: A review of challenges and opportunities. *Minerals Engineering*. 2023, 201, 108216. https://doi.org/10.1016/j.mineng.2023.108216
[35] Critical raw materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials, European Commission, 2010. https://www.eurominers.org/files/what-we-do/sustainable-development-issues/2010-report-critical-raw-materials-eu.pdf, Accessed March 4, 2025.
[36] Bulatovic SM. Flotation of Platinum Group Metal Ores. In: Bulatovic SM, ed. *Handbook of Flotation Reagents: Chemistry, Theory and Practice.* 1st ed. Amsterdam, Elsevier, 2010, 19-45. DOI:10.1016/B978-0-444-53082-0.00018-4.
[37] Glaister BJ, Mudd GM. The environmental costs of platinum–PGM mining and sustainability: Is the glass half-full or half-empty? *Minerals Engineering.* 2010, 23, 438-450. https://doi.org/10.1016/j.mineng.2009.12.007
[38] Wójcik M, Pawłowska B, Stachowicz F. Recycling of automotive catalytic converters with application of magneto-hydrodynamic pump. *Mechanika.* 2016, 88, 73-83. http://doi.prz.edu.pl/pl/pdf/mechanika/171
[39] Eurostat, End-of-life vehicle statistics. https://ec.europa.eu/eurostat/statistics-explained/index.php/End-of-life_vehicle_statistics#Total_number_of_end-of-life_vehicles Accessed March 4, 2025.
[40] Directive 2005/64/EC of the European Parliament and of the Council of 26 October 2005 on the type-approval of motor vehicles with regard to their reusability, recyclability and recoverability and amending Council Directive 70/156/EEC, European Parliament, Council of the European Union. *Official Journal of the European Union*. L 310/10. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32005L0064. Accessed March 4, 2025.
[41] Steinlechner S, Antrekowitsch J. Potential of a hydrometallurgical recycling process for catalysts to cover the demand for critical metals, like PGMs and cerium. *The Journal of the Minerals, Metals & Materials Society.* 2015, 67, 406-411. https://doi.org/10.1007/s11837-014-1263-x
[42] Saguru C, Ndlovu S, Moropeng D. A review of recent studies into hydrometallurgical methods for recovering PGMs from used catalytic converters. *Hydrometallurgy.* 2018, 182, 44-56. https://doi.org/10.1016/j.hydromet.2018.10.012
[43] Pawlak J, Lodyga-Chruscinska E, Chrustowicz J. Fate of platinum metals in the environment. *Journal of Trace Elements in Medicine and Biology.* 2014, 28, 247-254.

https://doi.org/10.1016/j.jtemb.2014.03.005
[44] Sen IS, Mitra A, Peucker-Ehrenbrink B, Rothenberg SE, Tripathi SN. Bizimis M. Emerging airborne contaminants in India: Platinum group elements from catalytic converters in motor vehicles. *Applied Geochemistry*. 2016, 75, 100-106. https://doi.org/10.1016/j.apgeochem.2016.10.006
[45] Wang Y, Li X. Health risk of platinum group elements from automobile catalysts. *Procedia Engineering.* 2012, 45, 1004-1009. https://doi.org/10.1016/j.proeng.2012.08.273
[46] Wiseman CLS, Pour ZH, Zereini F. Platinum group element and cerium concentrations in roadside environments in Toronto, Canada. *Chemosphere.* 2016, 145, 61-67. https://doi.org/10.1016/j.chemosphere.2015.11.056
[47] Martínez-Hernando M-P, García-Franco E, Bolonio D, Ortega MF, García-Martínez M-J. Life cycle sustainability assessment of the platinum supply chain in the European Union. *Sustainable Production and Consumption.* 2024, 46, 679-689. https://doi.org/10.1016/j.spc.2024.03.017
[48] International Platinum Group Metals Association (IPA), The Life Cycle Assessment of Platinum Group Metals Reference year 2022, April 2025. https://www.ipa-news.com/assets/contentimg/sustainability/ipa-lca-3-fact-sheet-final-april-2025.pdf. Accessed June 17, 2025.
[49] Hagelüken C, Goldmann D. Recycling and circular economy—towards a closed loop for metals in emerging clean technologies. *Mineral Economics*. 2022, 35, 539-562. https://doi.org/10.1007/s13563-022-00319-1
[50] Peng Z, Li Z, Lin X. Tang H, Ye L, Ma Y, Rao M, Zhang Y, Li G, Jiang T. Pyrometallurgical recovery of platinum group metals from spent catalysts. *The Journal of the Minerals, Metals & Materials Society.* 2017, 69, 1553-1562. https://doi.org/10.1007/s11837-017-2450-3
[51] D'yachkova AV, Kirillov AD, Alekseeva TY,.Karpov YA. Decomposition of samples of used ceramic based automotive catalytic converters in analytical autoclaves with resistive heating. *Inorganic Materials.* 2013, 49, 1272-1276. https://doi.org/10.1134/S0020168513140045
[52] Rumpold R, Antrekowitsch J. Recycling of platinum group metals from automotive catalysts by an acidic leaching process. In: *5th International Platinum Conference "A catalyst for change"*. Sun City, South Africa, 2012, pp. 695-714.
[53] Kim C-H, Woo SI, Jeon SH. Recovery of platinum-group metals from recycled automotive catalytic converters by carbochlorination. *Industrial & Engineering Chemistry Research.* 2000, 39, 1185-1192. https://doi.org/10.1021/ie9905355
[54] Shen S, Pan T, Liu X, Yuan L, Wang J, Zhang Y, Guo Z. Adsorption of Rh(III) complexes from chloride solutions obtained by leaching chlorinated spent automotive catalysts on ion-exchange resin Diaion WA21J. *Journal of Hazardous Materials.* 2010, 179, 104-112. https://doi.org/10.1016/j.jhazmat.2010.02.064
[55] Ghodrat M, Rhamdhani MA, Sharafi P, Samali B. A comparative life cycle assessment of recycling the platinum group metals from automobile catalytic converter: An Australian perspective. *Metallurgical and Materials Transactions E.* 2017, 4, 77-88. https://doi.org/10.1007/s40553-017-0109-1
[56] Ivanović SZ, Gorgievski MD, Božić DS, Trujuć VK, Mišić LjD. Removal of platinum group metals (PGMs) from the spent automobile catalyst by the pyrometallurgical process. In: *15th International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology".* Prague, Czech Republic, 2011, pp.701-704.
[57] Andersson M, Söderman ML, Sandén B.A. Are scarce metals in cars functionally recycled? *Waste Management*. 2017, 60, 407-416. https://doi.org/10.1016/j.wasman.2016.06.031
[58] Yakoumis I, Panou M, Moschovi AM, Panias D. Recovery of platinum group metals from spent automotive catalysts: A review. *Cleaner Engineering and Technology*. 2021, 3, 100112. https://doi.org/10.1016/j.clet.2021.100112
[59] Sasaki H, Maeda M. Zn-vapor pretreatment for acid leaching of platinum group metals from automotive catalytic converters. *Hydrometallurgy.* 2014, 147-148, 59-67. https://doi.org/10.1016/j.hydromet.2014.04.019
[60] Sun S, Jin C, He W, Li G, Zhu H, Huang J. Failure analysis of three-way catalysts through comprehensive characterization and understanding the role of pretreatment. *Journal of Environmental Chemical Engineering*. 2023, 11, 110414. https://doi.org/10.1016/j.jece.2023.110414
[61] Xolo L, Moleko-Boyce P, Makelane H, Faleni N, Tshentu Z.R. Status of Recovery of Strategic Metals from Spent Secondary Products. *Minerals.* 2021, 11, 673. https://doi.org/10.3390/min11070673
[62] Grilli ML, Slobozeanu AE, Larosa C, Paneva D, Yakoumis I, Cherkezova-Zheleva Z. Platinum Group Metals: Green Recovery from Spent Auto-Catalysts and Reuse in New Catalysts—A Review. *Crystals.* 2023, 13, 550. https://doi.org/10.3390/cryst13040550
[63] Hammadi MQ, Yassen RS, Abid KN. Recovery of platinum and palladium from scrap automotive catalytic converters. *Al-Khwarizmi Engineering Journal.* 2017, 13(3), 131-141. https://doi.org/10.22153/kej.2017.04.002
[64] Suoranta T, Zugazua O, Niemelä M, Perämäki P. Recovery of palladium, platinum, rhodium and ruthenium from catalyst materials using microwave-assisted leaching and cloud point extraction. *Hydrometallurgy.* 2015, 154, 56-62. https://doi.org/10.1016/j.hydromet.2015.03.014
[65] Atia AT, Spooren J, Fast microwave leaching of platinum, rhodium and cerium from spent non-milled autocatalyst monolith. *Chemical Engineering & Processing: Process Intensification.* 2021, 164, 108378 https://doi.org/10.1016/j.cep.2021.108378
[66] Nogueira CA, Paiva AP, Oliveira PC, Costa MC, Rosa da Costa AM. Oxidative leaching process with cupric ion in hydrochloric acid media for recovery of Pd and Rh from spent catalytic converters. *Journal of Hazardous Materials.* 2014, 278, 82-90. http://dx.doi.org/10.1016/j.jhazmat.2014.05.099
[67] Shin D, Park J, Jeong J, Kim B. A biological cyanide production and accumulation system and the recovery of platinum-group metals from spent automotive catalysts by biogenic cyanide. *Hydrometallurgy*. 2015, 158, 10-18. https://doi.org/10.1016/j.hydromet.2015.09.021
[68] Grilli ML, Slobozeanu AE, Larosa C, Paneva D, Yakoumis I, Cherkezova-Zheleva Z. Platinum Group Metals: Green Recovery from Spent Auto-Catalysts and Reuse in New Catalysts—A Review. *Crystals.* 2023, 13, 550. https://doi.org/10.3390/cryst13040550
[69] Binnemans K, Jones P.T. Solvometallurgy: An Emerging Branch of Extractive Metallurgy. *Journal of Sustainable Metallurgy.* 3, 2017, 570-600. https://doi.org/10.1007/s40831-017-0128-2
[70] Lee JY, Raju B, Kumar BN, Kumar JR, Park HK, Reddy BR. Solvent extraction separation and recovery of

palladium and platinum from chloride leach liquors of spent automobile catalyst. *Separation and Purification Technology.* 2010, 73, 213-218. https://doi.org/10.1016/j.seppur.2010.04.003
[71] Nguyen VT, Riaño S, Aktan E, Deferm C, Fransaer J, Binnemans K. Solvometallurgical Recovery of Platinum Group Metals from Spent Automotive Catalysts. *ACS Sustainable Chemical Engineering.* 2021, 9, 337-350. https://dx.doi.org/10.1021/acssuschemeng.0c07355
[72] Reddy BR, Raju B, Lee JY, Park HK. Process for the separation and recovery of palladium and platinum from spent automobile catalyst leach liquor using LIX 84I and Alamine 336. *Journal of Hazardous Materials.* 2010, 180, 253-258. https://doi.org/10.1016/j.jhazmat.2010.04.022
[73] Senthil K, Akiba U, Fujiwara K, Hamada F, Kondo Y. High selectivity and extractability of palladium from chloride leach liquors of an automotive catalyst residue by azothiacalix[4]arene derivative. *Hydrometallurgy.* 2017,169, 478-487. http://dx.doi.org/10.1016/j.hydromet.2017.02.016
[74] Ilyas S, Kim H, Srivastava RR. Separation of platinum group metals from model chloride solution using phosphonium-based ionic liquid. *Separation and Purification Technology.* 2022, 278, 119577. https://doi.org/10.1016/j.seppur.2021.119577

Izvod

ISTROŠENI AUTOKATALIZATORI OTPADNIH VOZILA KAO VREDAN IZVOR PLATINSKE GRUPE METALA

Ana Radojević, Jelena Jordanović, Tanja Kalinović, Jelena Kalinović, Snežana Šerbula

Univerzitet u Beogradu, Tehnički fakultet u Boru, Bor, Srbija

(PREGLEDNI RAD)
UDK: 546.91:[628.4.037:54-44
DOI: 10.5937/savteh2502005R

Svake godine u Evropi potrebno je pravilno upravljati sa više od 5 miliona vozila koja su na kraju svog veka upotrebe (*engl.* end-of-life vehicles, ELV), jer u suprotnom, neadekvatno rukovanje njima može dovesti do zagađenja životne sredine. Sa ekonomske tačke gledišta, oko 6 miliona tona materijala sa ekonomskom vrednošću se godišnje gubi sa ELV. Platina (Pt), paladijum (Pd) i rodijum (Rh) pripadaju platinskoj grupi metala (engl. platinum-group metals, PGM) i predstavljaju aktivnu komponentu autokatalizatora koji se koriste u cilju efikasne katalitičke konverzije izduvnih gasova u manje štetna jedinjenja. Automobilska industrija predstavlja jedan od sektora koji zahteva upotrebu velike količine resursa. Kako se broj motornih vozila povećava, na svetskom nivou postoji konstantna potražnja za navedenim plemenitim metalima, koji takođe spadaju i u kritične metale. Štaviše, metali platinske grupe koriste se u zelenim tehnologijama i to za elektrifikaciju motornih vozila, proizvodnju zelene energije i vodonika, itd. Zbog visokog sadržaja PGM, istrošeni autokatalizatori predstavljaju vredne sekundarne sirovine, koje se mogu iskoristiti sa nižim ulaganjima i sa manjim uticajem po životnu sredinu, u poređenju sa ekstrakcijom PGM iz ruda. U naučnoj literaturi predloženi su brojni agensi za luženje PGM, među kojima se favorizuju isplativa, ekološki prihvatljiva i održiva rešenja. Ovaj rad ima za cilj da naglasi važnost reciklaže PGM iz sekundarnih sirovina, pre svega istrošenih autokatalizatora (engl. automotive catalytic converters, ACCs) i da pruži jasan uvid u ključna pitanja vezana za trenutne globalne izazove ponude i potražnje za PGM.

Ključne reči: platinaska grupa metala, otpadna vozila, autokatalizatori, reciklaža

CRediT authorship contribution statement:
Ana Radojević: Conceptualization, Methodology, Investigation, Visualization, Writing – Original Draft
Jelena Jordanović: Visualization, Investigation
Tanja Kalinović: Validation, Writing – Reviewing and Editing
Jelena Kalinović: Validation, Writing – Reviewing and Editing
Snežana Šerbula: Validation, Writing – Reviewing and Editing